

S U M M A R Y

During the last few decades, organotin compounds have attracted wide attention of the organometallic chemists due to their versatile reactions, unique structural features and extensive commercial applications. The tin (IV) derivatives alone yield a great variety of structural types e.g. four-, five-, six-, seven- and eight-coordination at tin in neutral, cationic and anionic species. The commercial applications of organotin chemicals are equally impressing. Organotin compounds are possibly the best type of poly (vinyl chloride) stabilizers. Today, organotins are widely used as agricultural fungicides and miticides, industrial biocides, surface disinfectants, anthelmintics and marine antifouling agents. Apart from these, organotins have other uses.

The discovery of a novel synthetic route by Akzo Chemie group for the synthesis of β -carboalkoxy alkyl tin halides and related compounds has added a new dimension in the area of PVC stabilization. Lewis acidity of β -carboalkoxy alkyl tin compounds with varieties of mono- and polydentate ligands has not been explored significantly so far. The present investigation is concerned mainly with the preparation of different types of β -carboalkoxy alkyl tin complex compounds with a number of ligands and their

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characterization by elemental analysis and UV-Visible, IR and PMR spectral data.

In this dissertation, initially a very brief discussion on commercial applications of organotins has been presented. Thereafter, an attempt has been made to discuss the various Lewis acid types organotin coordination compounds, reported so far. The total number of such compounds is really very large and a vast number (more than hundred) of publications have appeared during the last few decades. The organotin moieties can form well characterised adducts and coordination complexes with ligands like pyridine, bi- and terpyridyl, 1,10-phenanthroline, pyridine-N-oxide, dimethyl sulphoxide and formamide, triorgano phosphine and arsine oxides, hexa-methyl phosphoric triamide, triazine, tetramethyl ethylene diamine, mono-, di- and triethanol amines, β -diketones, mono- and dithio carbamates, tropolone, kojic acid, xanthates, schiff bases, oximes, 8-hydroxy quinoline and its substituted derivatives, dithizone, diphenyl carbazone, substituted hydroxamic acids, amino acids etc.

The mono-, di- and tri-organotin moieties can form complexes of the types $RSnLX_2$, $RSnL_2X$, $RSnL_3$, R_2SnL_2 , R_2SnLX , R_3SnL etc (where R = alkyl or aryl groups, LH = ligands and X = halogen or pseudohalogen or other types of

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anions). Structural features of some of these complexes have been reported.

During the present investigation Lewis acidity of the following β -carboalkoxy ethyl tin chlorides and related compound have been studied.

1. Bis(β -carbomethoxy ethyl) tin dichloride
 $\left[(\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2)_2\text{SnCl}_2 \right]$
2. β -carbomethoxy ethyl tin trichloride $\left[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{SnCl}_3 \right]$
3. Bis(β -carbobutoxy ethyl)tin dichloride
 $\left[(\text{C}_4\text{H}_9\text{CO}_2\text{CH}_2\text{CH}_2)_2\text{SnCl}_2 \right]$
4. β -carbobutoxy ethyl tin trichloride
 $\left[\text{C}_4\text{H}_9\text{CO}_2\text{CH}_2\text{CH}_2\text{SnCl}_3 \right]$
5. β -carbomethoxy β' -methyl ethyl tin trichloride
 $\left[\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SnCl}_3 \right]$
6. α, α' -dimethyl β -acetyl ethyl tin trichloride
 $\left[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{SnCl}_3 \right]$

The ligands used are : (1) 8-hydroxy quinoline (Oxine), (2) 5,7-dichloro oxine, (3) 5,7-dibromo oxine (4) phenyl-5-azo oxine, (5) 5-(2'-carboxy phenyl)azo oxine, (6) 1,5-Diphenyl thiocarbazono (Dithizone), (7) 1,5-Diphenyl carbazono (8) Alizarin, (9) 1-nitroso-2-naphthol, (10) Quinalizarin and (11) Sodium Alizarin Sulphonate (Alizarin-s).

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Thirty seven new β -carboalkoxy ethyl tin complexes have been prepared and characterised. These are of the types: (1) R_2SnL_2 (where $R = CH_3CO_2CH_2CH_2^-$, $C_4H_9CO_2CH_2CH_2^-$; and $LH =$ Oxine, 5,7-dichloro oxine, 5,7-dibromo oxine, phenyl-5-azo oxine, 5 (2'-carboxy phenyl)azo oxine, dithizone), (2) R_2SnLX (where $R = CH_3CO_2CH_2CH_2^-$; $LH =$ oxine, dithizone, diphenyl carbazone, 1-nitroso-2-naphthol and $X = Cl, SCN$), (3) $RSnL_2X$ (where $R = CH_3CO_2CH_2CH_2^-$, $C_4H_9CO_2CH_2CH_2^-$, $CH_3CO_2CH(CH_3)CH_2^-$, $CH_3COCH_2C(CH_3)_2^-$; $LH =$ Oxine, 5,7-dichloro oxine, 5,7-dibromo oxine, phenyl-5-azo oxine, dithizone and $X = Cl, SCN$), (4) $RSnL_3$ (where $R = CH_3CO_2CH_2CH_2^-$, $C_4H_9CO_2CH_2CH_2^-$ and $LH =$ oxine, 5,7-dibromo oxine), (5) R_2SnL' (where $R = CH_3CO_2CH_2CH_2^-$, $C_4H_9CO_2CH_2CH_2^-$ and $L'H_2 =$ Alizarin) and (6) $RSnL'X$ (where $R = CH_3CO_2CH_2CH_2^-$, $C_4H_9CO_2CH_2CH_2^-$; $L'H_2 =$ Alizarin and $X = Cl$).

Attempts to prepare certain other β -carboalkoxy ethyl tin complexes with the ligands like oxine, 5,7-dichloro oxine, 5,7-dibromo oxine, dithizone, diphenyl carbazone, quinalizarin and sodium alizarin sulphate (Alizarin - S) have also been made. Although it was not possible to isolate the compounds in pure state, chelation of the ligands with the organotin moieties has been indicated from the IR spectra.

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In addition to complex compounds of β -carboalkoxy ethyl tin chlorides, attempts have been made to prepare some new derivatives of β -carboalkoxy ethyl tin compounds by replacing the chloride ions partially or completely by the groups like thiocyanate, azide, acetate etc. Two such thiocyanate derivatives have been obtained in crystalline state and characterised.

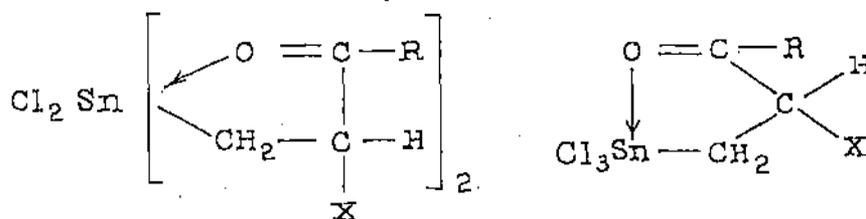
The complexes were prepared by reacting the solutions of β -carboalkoxy ethyl tin chlorides and the ligands in appropriate molar ratio. The liberated hydrochloric acid was neutralised with ammonia solution (17N) and the resulting ammonium chloride was removed by filtration. The filtrate was refluxed, concentrated and the complexes were isolated by fractional crystallization or similar techniques and then purified.

The electronic spectra of the β -carboalkoxy ethyl tin complexes in methanol show marked bathochromic shifts of the ligand bands in all cases. In case of oxinates the 310 nm band of free ligand shifts to 370-375 nm region, indicating strong chelation. The 324 nm band of 5,7-dichloro oxine shifts to 385-390 nm region in complexes and the 325 nm band of 5,7-dibromo oxine shifts to 388-390 nm region, in the corresponding complexes. In case of phenyl-5-azo oxine complexes, the shifting takes place from 380 nm to

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400-430 nm region. Dithizone shows a strong absorption band at 470 nm but in case of β -carboalkoxy ethyl tin dithizonates, the band is shifted to 480-503 nm region indicating chelation. Similar shifts of ligand bands are observed in β -carboalkoxy ethyl tin complexes of other ligands also.

In their IR spectra, the carbonyl stretching frequencies $\nu(\text{C}=\text{O})$ of the β -carboalkoxy ethyl tin chlorides lie between 1640-1680 cm^{-1} indicating internal coordination to the tin atom e.g.



(where R = OCH₃, OC₄H₉, CH₃ ; X = H, CH₃)

On complex formation with ligands, this internal coordination is partly or completely cleaved and the $\nu(\text{C}=\text{O})$ frequency shifts to $\sim 1725 \text{ cm}^{-1}$ showing the non-chelating nature of ester carbonyl group in the complexes. The cleavage of intramolecular carbonyl coordination is expected due to increased electron density to tin from the ligands. The shift is so marked that, in all cases it has been used as a guide for the formation of new complexes

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of β -carboalkoxy ethyl tin chlorides. Apart from this characteristic carbonyl frequency, modifications of other bands and appearance of some new characteristic bands have been identified to indicate clearly the formation of complexes. For example, the ν OH absorption of the ligands like oxine, substituted oxines, phenyl-5-azo oxine, alizarin etc. is found to be absent in the complexes. In case of dithizonate and diphenyl-carbazonate complexes, the presence of hydrogen bonded -NH frequency indicates the replacement of only one iminohydrogen out of two such hydrogen atoms of the ligand. The PMR spectra of these compounds also support this fact. The appearance of a broad band $\sim 1200 \text{ cm}^{-1}$ showed the presence of coupled NCS/NCO vibrations involved in coordination. The infrared spectra of alizarin complexes show that the two hydroxyl groups have been utilised in complex formation and possibly carbonyl groups do not involve in coordination to a marked degree. The stoichiometry of alizarin complexes are somewhat different from the complexes formed with other ligands.

The IR spectra of thiocyanato derivatives indicate that the thiocyanato group is attached to tin through the nitrogen atom as is generally observed. The IR spectral studies have contributed substantially and indication for chelation has been also obtained in certain cases where the pure compounds could not be isolated.

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From the integration of the curves in the PMR spectra of the β -carboalkoxy ethyl tin complexes, the ratio of different protons is found to be consistent with the composition of the complexes. In their PMR spectra, all the β -carboalkoxy ethyl tin chlorides exhibit three signals for α -CH₂ [H _{α}], β -CH₂ [H _{β}] and -OCH₃ or -OCH₂ [H_c] protons. In addition to these, the β -carboboxy ethyl tin chlorides exhibit two more signals, one for methylene protons (complex pattern) and the other for methyl protons, while β -carbomethoxy β' -methyl ethyl tin trichloride exhibits one more signal for methyl protons. On complex formation, in general all the alkyl protons exhibit shielding due to increased electron density in the tin atom via ligand donation. The α -methylene protons suffer maximum amount of shielding.

The chemical shifts observed for the ring protons in β -carboalkoxy ethyl tin oxinates and substituted oxinates show that the proton at 2-position (2-H) of quinoline ring is most effected. Deshielding and sometimes shielding is observed for 2-H protons while the other ring protons remains unaltered or slightly altered. In some oxine complexes the shielding of aromatic protons is observed, which is probably due to some steric reasons, while in all substituted oxinates deshielding of aromatic protons are observed in conformity with complex formation.

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Greater amount of deshielding for aromatic protons is obtained in case ^{of} chloro complexes in comparison to bis complexes, possibly due to the presence of Sn-Cl linkages.

In the PMR spectra of certain complexes, indication for the presence of geometrical isomers was obtained, though those could not be separated so far.

The reaction products obtained from α, α' -dimethyl β -acetyl ethyl tin trichloride with oxine presented certain difficulties in the proper characterisation of the products. One such product showed the presence of hydroxyl group and absence of any carbonyl group suggesting possible formation of complex from the enol form of α, α' -dimethyl β -acetyl ethyl tin trichloride, which of course will require further detailed studies for confirmation.

Preliminary evaluation of two β -carboalkoxy ethyl tin coordination compounds on the application as PVC stabilizers indicates some promise in that area. In the oven heat stability test, the compound Bis(β -carbomethoxy ethyl) tin bis-dithizonate shows a greater reserve of heat stability than the compound Bis(β -carbomethoxy ethyl) tin bis-oxinate and is comparable with the standard dibutyltin glycolate stabilizer. In respect to mill heat stability also, the dithizonate complex shows better performance than the oxinate complex.